Machine translation JP2003261699

(19) **Publication country** Japan Patent Office (JP)
(12) **Kind of official gazette** Open patent official report (A)
(11) **Publication No.** JP,2003-261699,A (P2003-261699A)
(43) **Date of Publication** September 19, Heisei 15 (2003. 9.19)
(54) **Title of the Invention** The etching reagent for liquid crystal polymers, and the etching approach using it
(51) **The 7th edition of International Patent Classification**

C08J 7/02 CFD
C09K 13/02
// C08L 67:00

FI

C08J 7/02 CFD A
C09K 13/02
C08L 67:00

Request for Examination Un-asking.
The number of claims 17
Mode of Application OL
Number of Pages 9
(21) **Application number** Application for patent 2002-64405 (P2002-64405)
(22) **Filing date** March 8, Heisei 14 (2002. 3.8)
(71) **Applicant**
Identification Number 000219314
Name Toray Industries Engineering
Address 3-3-3, Nakanoshima, Kita-ku, Osaka-shi, Osaka (Nakanoshima Mitsui building)
(71) **Applicant**
Identification Number 594066132
Name Raytech, Inc.
Address 1-103-54, Yoshinodai, Kawagoe-shi, Saitama-ken
(72) **Inventor(s)**
Name Akita Masanori
Address 1-1-45, Oe, Otsu-shi, Shiga-ken Inside of Toray Industries Engineering
(72) **Inventor(s)**
Name Oyama **
Address 11-13, Matsukazedai, Chigasaki-shi, Kanagawa-ken
(72) **Inventor(s)**
Name Kaneko Yoshiharu
Address 1-103-54, Yoshinodai, Kawagoe-shi, Saitama-ken Inside of Raytech, Inc.
Theme code (reference)

4F073

F term (reference)

4F073 AA06 BA25 BB01 EA01 EA11 EA21 EA22 EA24 EA55 EA62 HA04

(57) **Abstract**
Technical problem Offer the suitable etching reagent for etching of a liquid crystal polymer, and

its approach.

Means for Solution While alkali and the boiling point consist of a water-soluble fatty alcohol derivative and water 100 degrees C or more and water-soluble fatty alcohol or water-soluble aliphatic series amino alcohol is mentioned as said water-soluble fatty alcohol derivative, the glycols of 2-4 are mentioned as said water-soluble fatty alcohol, and, as for this etching reagent, the carbon number in a molecule is mentioned for monoethanolamine etc. as said water-soluble aliphatic series amino alcohol again.

Claim(s)

Claim 1 The etching reagent characterized by alkali and the boiling point consisting of a water-soluble fatty alcohol derivative and water 100 degrees C or more in the etching reagent for liquid crystal polymers.

Claim 2 The etching reagent according to claim 1 with which said alkali is characterized by said water-soluble fatty alcohol derivatives being **20 - 50 % of the weight and said water** 20 - 50% of the weight of presentation ratios ten to 40% of the weight.

Claim 3 The etching reagent according to claim 1 or 2 characterized by said water-soluble fatty alcohol derivative being water-soluble fatty alcohol.

Claim 4 The etching reagent according to claim 3 with which said water-soluble fatty alcohol is characterized by the carbon numbers in a molecule being the glycols of 2-4.

Claim 5 The etching reagent according to claim 4 characterized by said glycols being any one of ethylene glycol, propylene glycol, a butylene glycol, and the diethylene glycols.

Claim 6 The etching reagent according to claim 1 or 2 characterized by said water-soluble fatty alcohol derivative being water-soluble aliphatic series amino alcohol.

Claim 7 The etching reagent according to claim 6 characterized by said water-soluble aliphatic series amino alcohol being any one of monoethanolamine, diethanolamine, alpha-amino isopropanol, and the 2-amino butanols.

Claim 8 The etching reagent of any one publication of claim 1-7 characterized by said alkali being inorganic alkali.

Claim 9 The etching reagent of any one publication of claim 1-7 characterized by said alkali being organic alkali.

Claim 10 The etching reagent of any one publication of claim 1-7 characterized by said alkali being mixing with inorganic alkali and organic alkali.

Claim 11 The etching reagent according to claim 8 or 10 characterized by said inorganic alkali being an alkali-metal hydroxide or its carbonate.

Claim 12 The etching reagent according to claim 11 characterized by said alkali-metal hydroxide being a potassium hydroxide or a sodium hydroxide.

Claim 13 The etching reagent according to claim 9 or 10 characterized by said organic alkali being tetramethyl ammonium hydroxide or tetraethyl ammonium hydroxide.

Claim 14 The etching reagent according to claim 1 with which said water-soluble fatty alcohol derivative is monoethanolamine while said alkali is a potassium hydroxide, and said potassium hydroxide is characterized by said monoethanolamine being **20 - 40 % of the weight and said water** 20 - 55% of the weight of presentation ratios 25 to 40% of the weight.

Claim 15 The etching reagent of any one publication of claim 1-14 characterized by being the polymer to which said liquid crystal polymer has an ester bond in a molecule.

Claim 16 The etching reagent according to claim 15 characterized by the polymers which have an ester bond in said molecule being all aromatic polyester.

Claim 17 The etching approach characterized by etching a liquid crystal polymer by 50 degrees C - 90 degrees C solution temperature using the etching reagent of any one publication of claim 1-16.

Example Example 1 -- It was immersed in the etching reagent kept at 80 degrees C which consists of 28 % of the weight of potassium hydroxides, 33 % of the weight of monoethanolamines, and 39 % of the weight of water in the piece of a sample (magnitude is

5cmx5cm and thickness is 143 micrometers) of the one side copper-clad liquid crystal polymer base material (the thickness of 18 micrometers and liquid crystal polyester is 125 micrometers for copper thickness) by Japan Gore-Tex, Inc., and asked for thickness change of the liquid crystal polymer film which measured change of whole film thickness and be etched.

0041 In addition, it carried out, stirring an etching reagent in a beaker. The measurement result of thickness was as being shown in drawing 2 . The thickness of a liquid crystal polymer decreased with the passage of time, the liquid crystal polymer was completely etched in 20 minutes, and the copper front face was exposed. The decrement of the thickness of reaction time and a liquid crystal polymer was in proportionality, and the average of the etch rate of a liquid crystal polymer was a part for 6.4-micrometer/. Thickness is MITUTOYO. model made from CORP. It measured by 1 D-C112.

0042 Example 2 -- It was immersed in the etching reagent kept at 80 degrees C which consists of 40 % of the weight of potassium hydroxides, 40 % of the weight of propylene glycols, and 20 % of the weight of water in the piece of a sample (magnitude is 5cmx5cm and thickness is 143 micrometers) of the one side copper-clad liquid crystal polymer base material made from Gore-tex SUJAPAN, Inc. (the thickness of 18 micrometers and liquid crystal polyester is 125 micrometers for copper thickness), and asked for thickness change of the liquid crystal polymer film which measured change of whole film thickness and be etched.

0043 In addition, it carried out, stirring an etching reagent in a beaker. The measurement result of thickness was as being shown in drawing 2 . The thickness of a liquid crystal polymer decreased with the passage of time, the liquid crystal polymer was completely etched in 35 minutes, and the copper front face was exposed. The decrement of the thickness of reaction time and a liquid crystal polymer was in proportionality, and the average of the etch rate of a liquid crystal polymer was a part for 3.6-micrometer/. Thickness is MITUTOYO. model made from CORP. It measured by 1 D-C112. Thickness is MITUTOYO. model made from CORP. It measured by 1 D-C112.

0044 Example 3 -- It was immersed in the etching reagent kept at 80 degrees C which consists of 36 % of the weight of potassium hydroxides, 40 % of the weight of diethylene glycols, and 24 % of the weight of water in the piece of a sample (magnitude is 5cmx5cm and thickness is 143 micrometers) of the one side copper-clad liquid crystal polymer base material made from Gore-tex SUJAPAN, Inc. (the thickness of 18 micrometers and liquid crystal polyester is 125 micrometers for copper thickness), and asked for thickness change of the liquid crystal polymer film which measured change of whole film thickness and be etched.

0045 In addition, it carried out, stirring an etching reagent in a beaker. The measurement result of thickness was as being shown in drawing 2 . The thickness of a liquid crystal polymer decreased with the passage of time, the liquid crystal polymer was completely etched in 32 minutes, and the copper front face was exposed. The decrement of the thickness of reaction time and a liquid crystal polymer was in proportionality, and the average of the etch rate of a liquid crystal polymer was a part for 4-micrometer/. Thickness is MITUTOYO. It measured by model1 D-C112 made from CORP.

0046 Example 4 -- All surface etching was performed for the test piece of "ESP NEKKUSU (trade name) LCP" ("** KUTORA (trade name)":50 micrometer/Cu of a liquid-crystal-polymer film: 18 micrometers) by Nippon Steel chemistry incorporated company on the same conditions as an example 1, and change of film thickness was measured.

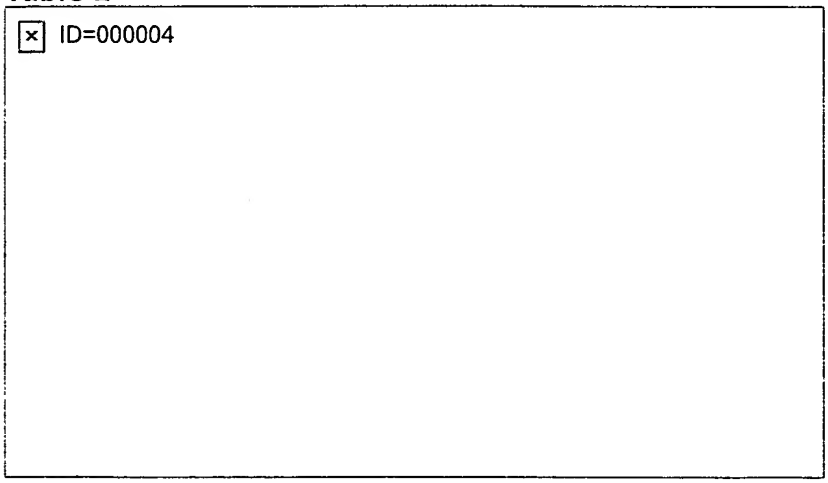
0047 The etch rate was a part for 1.6-micrometer/. It was later than the case of "BIAC" of Japan Gore-Tex, Inc. This is considered to be based on the difference in the structure of a polymer. Thickness is MITUTOYO. model made from CORP. It measured by 1 D-C112.

0048 Examples 1-6 of a comparison -- About the same base material as the base material of an example 1, the etching reagent was changed into 28%KOH water solution, a 1%KOH-80% ethanol water solution, a 17%KOH-36% ethanol water solution, and 7.3%KOH-5%BC one after another, and the etch rate was measured on the same conditions as the temperature conditions of an example 1. The result was as being shown in Table 2.

0049 The etch rate by 28%KOH water solution was a part for 0.7-micrometer/. Neither by ethanol nor the butyl-cellosolve system, when KOH concentration was high, in order for liquid separation to cause, 20% or more of solution was able to be adjusted.

0050 In the case of the 1%KOH-80% ethanol water solution, in the case of the 0.2-micrometerKOH **for // part 17%**-36% ethanol water solution, it was a part for 6-micrometer/, but the evaporation loss of liquid was intense, during processing, volume decreased sharply and

KOH concentration also changed sharply.
0051 On the other hand, with 7.3%KOH-5%BC liquid, although immersed for 10 minutes, etching hardly progressed. Moreover, in the case of the 17%KOH-36% ethanol water solution, the etch rate improved to same extent as examples 1 and 2, but after the reaction, evaporation of ethanol or moisture was so intense that volume decreased even to one half mostly during heating, and concentration change and an alcoholic odor were judged that it is difficult to use it industrially **it is intense and** .
0052 Example 5 -- One side copper-clad liquid crystal polymer base material by Japan Gore-Tex, Inc. (copper thickness 18 micrometers) the thickness of liquid crystal polyester -- the 125-micrometer piece of a sample (magnitude -- 5cmx -- 5cm) It was immersed in the etching reagent with which thickness was kept at 70 degrees C which consists of 28 % of the weight of potassium hydroxides, 33 % of the weight of ethanolamines, and 39 % of the weight of water in 143 micrometers for **5 minutes -** 20 minutes, and the decrement of the thickness of the liquid crystal polymer film which measured change of whole film thickness and was etched was calculated. Thickness is MITUTOYO. model made from CORP. It measured by 1 D-C112.
0053 In addition, it carried out, stirring an etching reagent in a beaker. The etch rate of the liquid crystal polymer for which it asked from measurement of thickness was a part for 3.4-micrometer/, and was one half mostly as compared with the etch rate of 80 degrees C.
0054 Example 6 -- One side copper-clad liquid crystal polymer base material made from Gore-tex SUJAPAN, Inc. (copper thickness 18 micrometers) the thickness of liquid crystal polyester -- the 125-micrometer piece of a sample (magnitude -- 5cmx -- 5cm) Thickness is immersed in the etching reagent kept at 80 degrees C which consists of 50 % of the weight and 50 % of the weight of ethanolamines of a tetramethyl AMMONYUMU hydroxide 25% water solution in 143 micrometers for **5 minutes -** 30 minutes, and measures change of whole film thickness. The decrement of the thickness of the etched liquid crystal polymer film was calculated.
0055 Thickness is MITUTOYO. model made from CORP. It measured by 1 D-C112. In addition, it carried out, stirring an etching reagent in a beaker. The etch rate of the liquid crystal polymer for which it asked from measurement of thickness was a part for 1.4-micrometer/, it was etched into homogeneity and the etching front face was smooth.
0056
Table 2



the inside of Table 2, and % -- weight % and "BIAC" -- the liquid crystal polymer of Japan Gore-Tex, Inc., and "VECTRA" -- the liquid crystal polymer of the copper-clad base material of Nippon Steel chemistry incorporated company, and KOH -- in propylene glycol and DEG, a diethylene glycol and EtOH show ethanol and, as for a potassium hydroxide and MEA, BC shows **monoethanolamine and PG** BUCHISERO, respectively. Moreover, in * mark of the example 3 of a comparison, ethanol and water evaporated during 80 degrees C and the processing for 30 minutes, and KOH at the time of termination was 29 % of the weight. Furthermore, ** mark of the example 4 of a comparison is the value calculated from change of the film thickness when processing for 20 minutes by the heterogeneous system as it is, although separated BC layer discolored brown.

0057 Change of thickness is shown in drawing 2 . Thickness change of illustration is change in above-mentioned examples 1-3 and the above-mentioned example 1 of a comparison. The a-c liquid and g liquid in drawing correspond to the a-c liquid and g liquid of Table 2.

0058 Example 7 -- The dry film was laminated to both sides of the piece of a sample (magnitude is 5cmx5cm and thickness is 143 micrometers) of the one side copper-clad liquid crystal polymer base material made from Gore-tex SUJAPAN, Inc. (for copper thickness, the thickness of 18 micrometers and liquid crystal polyester is 125 micrometers), exposure and development were performed using the pattern mask of a round hole as shown in a copper side at drawing 5 , and the resin pattern mask was produced. Copper etching was performed by ferric chloride and the copper mask pattern with a round hole was formed.

0059 Subsequently, this sample was etched for 23 minutes with the etching reagent kept at 80 degrees C which consists of 28% the % of the weight and 32 % of the weight of monoethanolamines of potassium hydroxides, and 40 % of the weight of water. When a dry film and a copper mask on the back were exfoliated, the liquid crystal film substrate which has a through beer hall as shown in drawing 6 was obtained.

0060 Example 8 -- The dry film was laminated in the liquid crystal film plane of the piece of a sample (magnitude is 5cmx5cm and thickness is 143 micrometers) of the one side copper-clad liquid crystal polymer base material made from Gore-tex SUJAPAN, Inc. (for copper thickness, the thickness of 18 micrometers and liquid crystal polyester is 125 micrometers), exposure and development were performed using the pattern mask of a round hole as shown in drawing 5 , and the resin pattern mask was produced.

0061 Subsequently, this sample was etched for 23 minutes with the etching reagent kept at 80 degrees C which consists of 28% the % of the weight and 32 % of the weight of monoethanolamines of potassium hydroxides, and 40 % of the weight of water. When the dry film and the copper mask were exfoliated, the copper-clad liquid crystal film substrate which has a blind beer hall as shown in drawing 7 was obtained.

0062 If alkali and the etching reagent concerning this invention to which the boiling point changes from a water-soluble fatty alcohol derivative and water 100 degrees C or more are used so that clearly **considering the result of an above-mentioned example and the example of a comparison** , a thermoplastic liquid crystal polymer can be etched comparatively easily, and the smooth nature of the etching side is also good.

0063 Since the chemical resistance of a liquid crystal polymer is high when alcoholic conventional system alkali etching liquid performs processing processing for a copper-clad liquid crystal polymer film base material, it is difficult for an etch rate to obtain the workpiece of a predetermined configuration late. However, according to the etching reagent concerning above-mentioned this invention, an etching side is smooth and can form easily an open hole (device hole) with the beer hall of a predetermined configuration, or a premature start lead etc. Also about the smooth nature of an etching side, the effectiveness that you may set to flow plating processing of a through hole or a blind beer hall is expectable.

---

[x] ID=000002

DETAILED DESCRIPTION

Detailed Description of the Invention

0001

Field of the Invention This invention relates to the etching approach of using the etching reagent for liquid crystal polymers, and it.

0002

Description of the Prior Art Practical use is widely presented with the copper-clad polyimide film base material former as everyone knows as a base material a flexible printed circuit board, TAB and CSP, or for hard disk drives.

0003 namely, -- forming a metal wiring circuit in it **** -- being certain -- it is -- although a through hole, a beer hall like a blind hole or a device hole, etc. is formed and practical use is presented, since it is difficult to form the device hole in which wiring like a premature start lead was formed, and a beer hall, plasma etching and liquid etching are liked by punching and laser etching.

0004 On the other hand, although thermal resistance is excellent with a miniaturization and highly-precise-izing of electronic equipment, since absorptivity is large, the fault of the copper-clad polyimide film base material that dimensional accuracy will fall in response to the effect of humidity conditions comes to be regarded as questionable, for the reason, it has the thermal resistance demanded at the time of a soldered joint instead of a copper-clad polyimide film base material, and the liquid crystal polymer which whose absorptivity is small and is moreover excellent in dimensional accuracy nature has come to be used.

0005 However, the molecular structure is upright liquid crystal structure, and since chemical resistance has neither absorptivity nor a hydrophilic property highly, by general liquid etching, processing of a detailed device hole, a beer hall, etc. is difficult for the liquid crystal polymer represented with liquid crystal polyester. For example, even if it etches the polyethylene terephthalate which is general-purpose polyester resin in the caustic alkali water solution widely used for etching processing of surface treatment etc. from the former, an etch rate is slow and does not deserve practical use.

0006 Moreover, for example, although the polyimide etching reagent which Du Pont (U.S.) has proposed in JP,58-103531,B is an inorganic alkali system etching reagent of content of the low-boiling point alcohol and the caustic alkali which are represented by ethanol and propanol, and the etch rate of this liquid improves, during etching, low-boiling point alcohol evaporates and a liquid presentation changes.

0007 If etching temperature is lowered in order that uniform etching by which whose adjustment of liquid concentration was very troublesome and was stabilized may be difficult and may control change of liquid concentration since an etch rate changes with the passage of time for the reason, since an etch rate will fall quickly, it is difficult to use it for industrial etching processing of a liquid

crystal polymer.
0008 So, although laser etching had to be applied to the copper-clad liquid crystal polymer film base material or the liquid crystal polymer film base material as simple substance material, and a liquid crystal polymer is thermoplasticity, it is difficult for the circuit pattern by heat, deformation of a hole configuration, etc. to occur, to become in equipment and large-sized, while pattern formation with a smooth front face is difficult, and to use for a sake industrially.
0009 In addition, when making many holes, and making a large hole especially, it also has the fault that etching time becomes long and cost becomes high. Thus, each conventional etching technique reaches technically and is not suitable to the liquid crystal polymer on economical efficiency or quality.
0010
Problem(s) to be Solved by the Invention This invention is invented in view of an above-mentioned fault, and the purpose is offering a suitable etching reagent etching etching of a liquid crystal polymer, and the metal flare liquid crystal polymer film base material and the liquid crystal polymer film base material as simple substance material which carried out thermocompression bonding of a liquid crystal polymer film and the metallic foils (for example, copper foil etc.) especially, and the etching approach.
0011
Means for Solving the Problem In order to solve the above-mentioned technical problem, in the etching reagent for liquid crystal polymers concerning this invention, alkali and the boiling point are using a water-soluble fatty alcohol derivative and water 100 degrees C or more as the presentation component.
0012 Thus, since alkali and the boiling point contain the water-soluble fatty alcohol derivative 100 degrees C or more, a liquid crystal polymer (for example, polyester system liquid crystal polymer) can be etched comparatively easily, and in etching of a metal flare liquid crystal polymer film base material, the workpiece which is stabilized, can form a device hole, a beer hall, etc. and has a smooth etching front face can be obtained, without doing fatal damage to metal wire patterns other than a liquid crystal polymer etc.
0013 Moreover, in the etching approach of the liquid crystal polymer concerning this invention, the temperature of an above-mentioned etching reagent is kept at 50 degrees C - 90 degrees C, and is etched. For the reason, while being able to obtain an economical etch rate, too much change of liquid concentration can be prevented.
0014 In addition, as for the presentation ratio of an above-mentioned etching reagent, it is desirable that a water-soluble fatty alcohol derivative 100 degrees C or more is **alkali / 20 - 50 % of the weight and water** 20 - 50 % of the weight for 10 - 40 % of the weight and the boiling point. Moreover, the boiling point of a water-soluble fatty alcohol derivative 100 degrees C or more may be any of water-soluble fatty alcohol or water-soluble aliphatic series amino alcohol. Moreover, although alkali may be any of inorganic alkali, organic alkali, or those mixing, generally inorganic alkali is chosen.
0015
Embodiment of the Invention The etching reagent concerning this invention is a thing for etching a liquid crystal polymer, and alkali and the boiling point of the presentation component are water-soluble fatty alcohol derivatives and water 100 degrees C or more.
0016 While this alkali may be any of inorganic alkali, organic alkali, or those mixing, the gestalt may also be any of a solid or a water solution. A water solution is desirable when using industrially. Moreover, mixing of both alkali is suitable when controlling a reaction rate to predetermined.
0017 As an example of inorganic alkali, alkali metal, such as a potassium hydroxide and a sodium hydroxide, and the carbonate of those are mentioned. Moreover, tetramethyl ammonium hydroxide and tetraethyl ammonium hydroxide are mentioned as an example of organic alkali. Although above-mentioned organic alkali generates an amine compound with heating of 100 degrees C or less in many cases, since inorganic alkali does not have such a thing even if it heats it, generally it is desirable to choose this.
0018 Moreover, the boiling point may be **the boiling point of a water-soluble fatty alcohol derivative 100 degrees C or more** any of water-soluble fatty alcohol 100 degrees C or more or water-soluble aliphatic series amino alcohol, and the glycols of 2-4 are mentioned for carbon numbers, such as ethylene glycol, propylene glycol, a butylene glycol, and a diethylene glycol, as

an example of water-soluble fatty alcohol. What, on the other hand, has the alkyl group whose carbon numbers, such as monoethanolamine, diethanolamine, alpha-amino isopropanol, and 2-amino butanol, are two to about four as an example of water-soluble aliphatic series amino alcohol is mentioned.

0019 Water-soluble fatty alcohol derivatives, such as these amino alcohol, glycols, etc., have good compatibility with the water solution of inorganic alkali or organic alkali, and it can mix them to homogeneity by the ratio of arbitration in the limitation which is not high concentration extremely. Although ethanol and butoxy ethanol (BUCHISERO) which are generally industrially used widely as alcohol to it have very high compatibility with water, when both are mixed, they are difficult for layer separation of liquid to occur and to adjust a uniform solution.

0020 Moreover, although it is thought that inorganic **above-mentioned** or an organic alkali water solution has the operation which hydrolyzes liquid crystal polyester, since **its** there is no wettability, an etch rate is very small **the water resisting property of a liquid crystal polymer is high, and** , if independent.

0021 However, in this invention, since the boiling point has put a water-soluble fatty alcohol derivative and alkali 100 degrees C or more together, the etch rate of liquid crystal polyester can be raised remarkably. This is considered because this water-soluble fatty alcohol derivative promotes the wettability of inorganic **in a liquid crystal polymer front face** , or an organic alkali component, and permeability, and a hydrolysis reaction is sped up and there are elution and an operation to remove from a resin front face about the hydrolysis product of liquid crystal polyester.

0022 In addition, a water-soluble fatty alcohol derivative is not limited to using only one belonging to it, but two or more may be mixed and used for it. Since water solubility falls and compatibility with an alkali water solution worsens as a carbon number generally increases, a 4 or less-about thing has **water-soluble fatty alcohol** a desirable carbon number.

0023 Moreover, water-soluble fatty alcohol is easily removable together with an alkali component by rinsing after etching (it does not ask whether it is molten-bath washing). The boiling point is as high as 150 degrees C or more, and the permeability to liquid crystal polyester and its solubility of a hydrolysis product are also high, and since especially the monoethanolamine that is one of water-soluble aliphatic series amino alcohol or the water-soluble aliphatic series amino alcohol can moreover come to hand easily industrially, it is desirable.

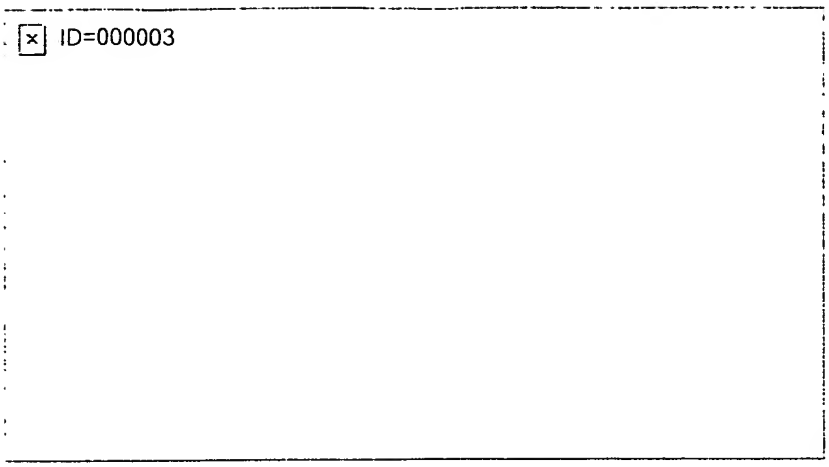
0024 Although an above-mentioned etching reagent is used in order to etch a liquid crystal polymer, this liquid crystal polymer may be prepared in what kind of gestalt. Generally, it is prepared in the gestalt of the metal flare liquid crystal polymer film base material which carried out thermocompression bonding of a liquid crystal polymer film and the metallic foils (for example, copper foil etc.), or the liquid crystal polymer film base material as simple substance material.

0025 Although the polyester resin base material obtained by copolymerization of the aromatic compound monomer which has a hydroxyl group and a carboxyl group is mentioned into a molecule as an example of representation of this liquid crystal polymer film base material, the molecular structure of this is shown in drawing 1 .

0026 Moreover, the liquid crystal polyester marketed is shown in Table 1. These are aromatic series liquid crystal polyester. They are EKONORU (trade name) of Sumitomo Chemical Co., Ltd., VECTRA of Kuraray Co., Ltd., etc. The liquid crystal polyester used for the copper-clad base material of Japan Gore-Tex in addition to these is mentioned.

0027

Table 1



moreover, as a copper-clad liquid crystal polymer film base material which carried out thermocompression bonding of an above-mentioned liquid crystal polymer film and copper foil, "BIAC" (copper-clad liquid crystal polymer film base material) of Japan Gore-Tex, the "LCP ESP NEKKUSU L series (VECTRA is used) of Nippon Steel chemistry incorporated company, etc. are mentioned.

0028 In addition, since the circuit board used as an electronic-parts ingredient of a pocket device or a household-electric-appliances device is set like processing or an erector and a soldered joint is performed in many cases, only the thermal resistance which can bear it is required. In spite of being thermoplasticity, a thing 200 degrees C or more has much heat deflection temperature, and since all aromatic series mold liquid crystal polyester is excellent in dimensional stability or an electrical property, it is the ingredient which was extremely excellent as an electronic-parts ingredient more than the polyimide ingredient. However, all aromatic series mold liquid crystal polyester has high chemical resistance, and since absorptivity is small, in general alkali etching, etching into a predetermined configuration is very difficult for it.

0029 moreover, in processing the electronic parts in which patterns, such as metal wiring, a beer hall, and a device hole, were formed, generally Although the dry film and liquefied resist of copper foil or an alkali development mold are used in many cases, as a pattern mask ingredient these resin resistance **as opposed to alkali as the name suggests** -- there is nothing -- since it is weak in an alkali water solution especially -- warming -- it is frequent to become the cause by which exfoliation of the resin film for masks occurs during etching, an etching reagent permeates between a metal thin film and mask resin, and an undercut is produced.

0030 Therefore, when etching a liquid crystal polyester ingredient, in order to obtain the pattern of a predetermined configuration, fully considering is important not only for the etching engine performance of a liquid crystal polymer but relation with a mask ingredient, and it is necessary to manage appropriately not only alkali concentration but the concentration and moisture concentration of alcohols which live together.

0031 the mixing ratio of inorganic alkali, a water-soluble fatty alcohol derivative, and water -- about 33 % of the weight has **about one, i.e., inorganic alkali, / a water-soluble fatty alcohol derivative** the most desirable **a rate / water / 1 and** fatty alcohol derivative **water-soluble** 33% of the weight 33% of the weight at a weight ratio water to inorganic alkali-1. Generally, if an inorganic alkali component becomes 20 or less % of the weight, an etch rate will become slow, and if 40 % of the weight is exceeded, an inorganic alkali component will dissociate in many cases. However, in the case of organic alkali, an alkali component should just be 10 % of the weight or more.

0032 On the other hand, since an alcoholic component is removed raising the hydrophilic property of the front face of a liquid crystal polymer at the time of an etching reaction, and dissolving the hydrolysis product of a liquid crystal polymer moderately, it does so the effectiveness which makes an etching front face smooth. Therefore, if alcoholic components run short and it becomes 20 or less % of the weight, since the ratio of water will increase, hydrolysis becomes unstable and moderate exfoliation removal of a surface hydrolysis product is checked.

0033 therefore, hydrolysis of liquid crystal -- an ununiformity -- becoming -- that it will be in a

surface state the bottom coarsely **** -- being certain -- it is -- an etching residue increases, the configuration of an etching part tends to become unstable, and if an alcoholic component decreases when etching especially using a dry film mask, since mask exfoliation will occur, etching into predetermined becomes difficult.

0034 Moreover, if it becomes 40% of the weight or more, since the ratio of water will decrease, the solubility of a potassium hydroxide worsens and causes precipitation. For the reason, for inorganic alkali, a water-soluble fatty alcohol derivative is **the water of the fitness concentration of each presentation component in an etching reagent** about 20 - 60 % of the weight 20 to 40% of the weight 20 to 40% of the weight.

0035 The etch rate of the etching reagent concerning this invention is quicker as compared with it of the conventional inorganic alkali water solution, and when concentration is the same conditions, it is about 10 times quick, so that clearly **considering the table 2 showing the result of the below-mentioned example and the example of a comparison** .

0036 Moreover, although the inclination for an etch rate to improve will be seen by using a water solution as an ethanol water solution if only an etch rate is measured Since the solubility of the inorganic alkali (for example, hydroxylation alkali) to an ethanol water solution is small, if the inorganic alkali concentration in liquid is raised In order that alkali concentration must be made low since layer separation is caused, the ethanol of a low-boiling point may evaporate and a presentation may change during the pyrogenetic reaction of etching upwards, a rate of reaction changes and uniform etching becomes difficult in pattern formation etc.

0037 In addition, amounts, such as the amount of alkali in an etching reagent and monoethanolamine, are manageable by carrying out potentiometric titration with the hydrochloric acid of normality. Whenever **in etching / solution temperature** is 60 degrees C - 90 degrees C (preferably 80 degrees C), and 1 minute - the 30-minute about room of etching time is desirable. If temperature is low, reaction time will start, if it becomes an elevated temperature not much, evaporation of moisture or alcohols will become intense and liquid concentration will tend to change. When using organic alkali, if it is made an elevated temperature, since odor generating from an organic alkali component becomes strong, it is not so desirable from the field on work environment.

0038 As an approach of contacting an above-mentioned base material and an above-mentioned etching reagent, you may be which approaches, such as an approach immersed in a base material into the liquid of a stirring condition, the approach of injecting liquid to a base material, a method of hitting a jet blast in liquid, and the approach of irradiating a supersonic wave in liquid. When making it contact in liquid, it is desirable to rock a base material.

0039 Although the through beer hall and the blind beer hall were processed into the liquid crystal polymer using the etching reagent concerning this invention, while the SEM (Scanning Electron Microscope) photograph of the obtained through beer hall is shown in drawing 8 and 9, the SEM photograph of a blind beer hall is shown in drawing 10 and 11. Also in any, it turns out that the liquid crystal polymer of the hole side-attachment-wall section is removed finely, and neither a crack nor big irregularity is also in an etching front face, and it has become a comparatively smooth front face.

0040

Example Example 1 -- It was immersed in the etching reagent kept at 80 degrees C which consists of 28 % of the weight of potassium hydroxides, 33 % of the weight of monoethanolamines, and 39 % of the weight of water in the piece of a sample (magnitude is 5cmx5cm and thickness is 143 micrometers) of the one side copper-clad liquid crystal polymer base material (the thickness of 18 micrometers and liquid crystal polyester is 125 micrometers for copper thickness) by Japan Gore-Tex, Inc., and asked for thickness change of the liquid crystal polymer film which measured change of whole film thickness and be etched.

0041 In addition, it carried out, stirring an etching reagent in a beaker. The measurement result of thickness was as being shown in drawing 2 . The thickness of a liquid crystal polymer decreased with the passage of time, the liquid crystal polymer was completely etched in 20 minutes, and the copper front face was exposed. The decrement of the thickness of reaction time and a liquid crystal polymer was in proportionality, and the average of the etch rate of a liquid crystal polymer was a part for 6.4-micrometer/. Thickness is MITUTOYO. model made from CORP. It measured by 1 D-C112.

0042 Example 2 -- It was immersed in the etching reagent kept at 80 degrees C which consists of 40 % of the weight of potassium hydroxides, 40 % of the weight of propylene glycols, and 20 % of the weight of water in the piece of a sample (magnitude is 5cmx5cm and thickness is 143 micrometers) of the one side copper-clad liquid crystal polymer base material made from Gore-tex SUJAPAN, Inc. (the thickness of 18 micrometers and liquid crystal polyester is 125 micrometers for copper thickness), and asked for thickness change of the liquid crystal polymer film which measured change of whole film thickness and be etched.
0043 In addition, it carried out, stirring an etching reagent in a beaker. The measurement result of thickness was as being shown in drawing 2 . The thickness of a liquid crystal polymer decreased with the passage of time, the liquid crystal polymer was completely etched in 35 minutes, and the copper front face was exposed. The decrement of the thickness of reaction time and a liquid crystal polymer was in proportionality, and the average of the etch rate of a liquid crystal polymer was a part for 3.6-micrometer/. Thickness is MITUTOYO. model made from CORP. It measured by 1 D-C112. Thickness is MITUTOYO. model made from CORP. It measured by 1 D-C112.
0044 Example 3 -- It was immersed in the etching reagent kept at 80 degrees C which consists of 36 % of the weight of potassium hydroxides, 40 % of the weight of diethylene glycols, and 24 % of the weight of water in the piece of a sample (magnitude is 5cmx5cm and thickness is 143 micrometers) of the one side copper-clad liquid crystal polymer base material made from Gore-tex SUJAPAN, Inc. (the thickness of 18 micrometers and liquid crystal polyester is 125 micrometers for copper thickness), and asked for thickness change of the liquid crystal polymer film which measured change of whole film thickness and be etched.
0045 In addition, it carried out, stirring an etching reagent in a beaker. The measurement result of thickness was as being shown in drawing 2 . The thickness of a liquid crystal polymer decreased with the passage of time, the liquid crystal polymer was completely etched in 32 minutes, and the copper front face was exposed. The decrement of the thickness of reaction time and a liquid crystal polymer was in proportionality, and the average of the etch rate of a liquid crystal polymer was a part for 4-micrometer/. Thickness is MITUTOYO. It measured by model1 D-C112 made from CORP.
0046 Example 4 -- All surface etching was performed for the test piece of "ESP NEKKUSU (trade name) LCP" ("** KUTORA (trade name)":50 micrometer/Cu of a liquid-crystal-polymer film: 18 micrometers) by Nippon Steel chemistry incorporated company on the same conditions as an example 1, and change of film thickness was measured.
0047 The etch rate was a part for 1.6-micrometer/. It was later than the case of "BIAC" of Japan Gore-Tex, Inc. This is considered to be based on the difference in the structure of a polymer. Thickness is MITUTOYO. model made from CORP. It measured by 1 D-C112.
0048 Examples 1-6 of a comparison -- About the same base material as the base material of an example 1, the etching reagent was changed into 28%KOH water solution, a 1%KOH-80% ethanol water solution, a 17%KOH-36% ethanol water solution, and 7.3%KOH-5%BC one after another, and the etch rate was measured on the same conditions as the temperature conditions of an example 1. The result was as being shown in Table 2.
0049 The etch rate by 28%KOH water solution was a part for 0.7-micrometer/. Neither by ethanol nor the butyl-cellosolve system, when KOH concentration was high, in order for liquid separation to cause, 20% or more of solution was able to be adjusted.
0050 In the case of the 1%KOH-80% ethanol water solution, in the case of the 0.2-micrometerKOH **for // part 17%**-36% ethanol water solution, it was a part for 6-micrometer/, but the evaporation loss of liquid was intense, during processing, volume decreased sharply and KOH concentration also changed sharply.
0051 On the other hand, with 7.3%KOH-5%BC liquid, although immersed for 10 minutes, etching hardly progressed. Moreover, in the case of the 17%KOH-36% ethanol water solution, the etch rate improved to same extent as examples 1 and 2, but after the reaction, evaporation of ethanol or moisture was so intense that volume decreased even to one half mostly during heating, and concentration change and an alcoholic odor were judged that it is difficult to use it industrially **it is intense and** .
0052 Example 5 -- One side copper-clad liquid crystal polymer base material by Japan Gore-Tex, Inc. (copper thickness 18 micrometers) the thickness of liquid crystal polyester -- the 125-micrometer piece of a sample (magnitude -- 5cmx -- 5cm) It was immersed in the etching reagent with which thickness was kept at 70 degrees C which consists of 28 % of the weight of potassium

hydroxides, 33 % of the weight of ethanolamines, and 39 % of the weight of water in 143 micrometers for **5 minutes -** 20 minutes, and the decrement of the thickness of the liquid crystal polymer film which measured change of whole film thickness and was etched was calculated. Thickness is MITUTOYO. model made from CORP. It measured by 1 D-C112.

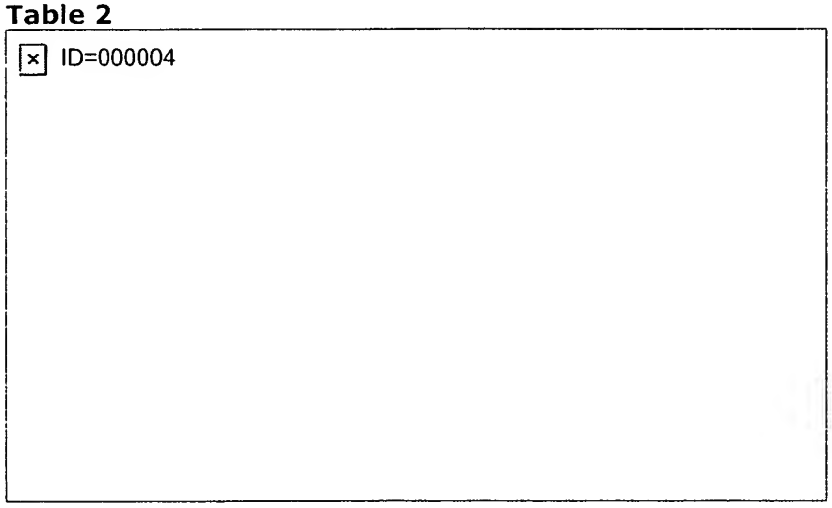
0053 In addition, it carried out, stirring an etching reagent in a beaker. The etch rate of the liquid crystal polymer for which it asked from measurement of thickness was a part for 3.4-micrometer/, and was one half mostly as compared with the etch rate of 80 degrees C.

0054 Example 6 -- One side copper-clad liquid crystal polymer base material made from Gore-tex SUJAPAN, Inc. (copper thickness 18 micrometers) the thickness of liquid crystal polyester -- the 125-micrometer piece of a sample (magnitude -- 5cmx -- 5cm) Thickness is immersed in the etching reagent kept at 80 degrees C which consists of 50 % of the weight and 50 % of the weight of ethanolamines of a tetramethyl AMMONYUMU hydroxide 25% water solution in 143 micrometers for **5 minutes -** 30 minutes, and measures change of whole film thickness. The decrement of the thickness of the etched liquid crystal polymer film was calculated.

0055 Thickness is MITUTOYO. model made from CORP. It measured by 1 D-C112. In addition, it carried out, stirring an etching reagent in a beaker. The etch rate of the liquid crystal polymer for which it asked from measurement of thickness was a part for 1.4-micrometer/, it was etched into homogeneity and the etching front face was smooth.

0056

Table 2



the inside of Table 2, and % -- weight % and "BIAC" -- the liquid crystal polymer of Japan Gore-Tex, Inc., and "VECTRA" -- the liquid crystal polymer of the copper-clad base material of Nippon Steel chemistry incorporated company, and KOH -- in propylene glycol and DEG, a diethylene glycol and EtOH show ethanol and, as for a potassium hydroxide and MEA, BC shows **monoethanolamine and PG** BUCHISERO, respectively. Moreover, in * mark of the example 3 of a comparison, ethanol and water evaporated during 80 degrees C and the processing for 30 minutes, and KOH at the time of termination was 29 % of the weight. Furthermore, ** mark of the example 4 of a comparison is the value calculated from change of the film thickness when processing for 20 minutes by the heterogeneous system as it is, although separated BC layer discolored brown.

0057 Change of thickness is shown in drawing 2 . Thickness change of illustration is change in above-mentioned examples 1-3 and the above-mentioned example 1 of a comparison. The a-c liquid and g liquid in drawing correspond to the a-c liquid and g liquid of Table 2.

0058 Example 7 -- The dry film was laminated to both sides of the piece of a sample (magnitude is 5cmx5cm and thickness is 143 micrometers) of the one side copper-clad liquid crystal polymer base material made from Gore-tex SUJAPAN, Inc. (for copper thickness, the thickness of 18 micrometers and liquid crystal polyester is 125 micrometers), exposure and development were performed using the pattern mask of a round hole as shown in a copper side at drawing 5 , and the resin pattern mask was produced. Copper etching was performed by ferric chloride and the copper mask pattern with a round hole was formed.

0059 Subsequently, this sample was etched for 23 minutes with the etching reagent kept at 80

degrees C which consists of 28% the % of the weight and 32 % of the weight of monoethanolamines of potassium hydroxides, and 40 % of the weight of water. When a dry film and a copper mask on the back were exfoliated, the liquid crystal film substrate which has a through beer hall as shown in drawing 6 was obtained.

0060 Example 8 -- The dry film was laminated in the liquid crystal film plane of the piece of a sample (magnitude is 5cmx5cm and thickness is 143 micrometers) of the one side copper-clad liquid crystal polymer base material made from Gore-tex SUJAPAN, Inc. (for copper thickness, the thickness of 18 micrometers and liquid crystal polyester is 125 micrometers), exposure and development were performed using the pattern mask of a round hole as shown in drawing 5 , and the resin pattern mask was produced.

0061 Subsequently, this sample was etched for 23 minutes with the etching reagent kept at 80 degrees C which consists of 28% the % of the weight and 32 % of the weight of monoethanolamines of potassium hydroxides, and 40 % of the weight of water. When the dry film and the copper mask were exfoliated, the copper-clad liquid crystal film substrate which has a blind beer hall as shown in drawing 7 was obtained.

0062 If alkali and the etching reagent concerning this invention to which the boiling point changes from a water-soluble fatty alcohol derivative and water 100 degrees C or more are used so that clearly **considering the result of an above-mentioned example and the example of a comparison** , a thermoplastic liquid crystal polymer can be etched comparatively easily, and the smooth nature of the etching side is also good.

0063 Since the chemical resistance of a liquid crystal polymer is high when alcoholic conventional system alkali etching liquid performs processing processing for a copper-clad liquid crystal polymer film base material, it is difficult for an etch rate to obtain the workpiece of a predetermined configuration late. However, according to the etching reagent concerning above-mentioned this invention, an etching side is smooth and can form easily an open hole (device hole) with the beer hall of a predetermined configuration, or a premature start lead etc. Also about the smooth nature of an etching side, the effectiveness that you may set to flow plating processing of a through hole or a blind beer hall is expectable.

0064

Effect of the Invention According to this invention, like ****, a suitable etching reagent to etch etching of a liquid crystal polymer, and the metal flare liquid crystal polymer film base material and the liquid crystal polymer film base material as simple substance material which carried out thermocompression bonding of a liquid crystal polymer film and the metallic foils (for example, copper foil etc.) especially, and the etching approach can be acquired.